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Gas/solid displacement reactions have been examined as a means of altering the chemistry of bioclastic silica structures (e.g., the self-assembled microshells of diatoms, a type of aquatic algae) into other ceramic compositions. Complex-shaped silica microshells with nanoscale features were exposed to Mg(g) at <900oC. The silica microshells underwent the following net displacement reaction: $2Mg(g) + SiO2(s) => 2MgO(s) + \{Si\}$ (1) where {Si} refers to silicon dissolved within a Mg-Si liquid. The Mg-Si liquid, which formed by the continued reaction of excess Mg(g) with reduced Si, was observed to sweat away from the solid MgO product of this reaction at 900oC to yield Si-free micro/nanostructures. The resulting MgO structures retained the 3-D shapes and fine features of the starting diatom microshells. This demonstration of shape-preserving chemical conversion opens the door to a wide variety of other chemical conversion reactions that we have begun to examine.

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AFOSR Final Performance Report

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Objective: To examine the near net-shape chemical conversion of biosilica nanoparticle structures via the BaSIC (Bioclastic and Shape-preserving Inorganic Conversion) process.

Approach and Key Results:

Gas/solid displacement reactions have been examined as a means of altering the chemistry of bioclastic silica structures (e.g., the self-assembled microshells of diatoms, a type of aquatic algae) into other ceramic compositions. Complex-shaped silica microshells with nanoscale features were exposed to Mg(g) at ≤900°C. The silica microshells underwent the following net displacement reaction:

$$2Mg(g) + SiO_2(s) => 2MgO(s) + \{Si\} \quad (1)$$

where {Si} refers to silicon dissolved within a Mg-Si liquid. The Mg-Si liquid, which formed by the continued reaction of excess Mg(g) with reduced Si, was observed to sweat away from the solid MgO product of this reaction at 900°C to yield Si-free micro/nanostructures. The resulting MgO structures retained the 3-D shapes and fine features of the starting diatom microshells. This demonstration of shape-preserving chemical conversion opens the door to a wide variety of other chemical conversion reactions that we have begun to examine.

Conclusions:

Diatoms are but one of numerous natural microorganisms that are capable of assembling complex, 3-D structures (microshells) comprised of solid nanoparticles. The ability of a given diatom species to generate microshells of precisely the same shape and with the same nanoscale features upon reproduction strongly suggests that such self-assembly is under genetic control. While a wide variety of 3-D shapes and features can be found among the 10^4-10^5 extant diatom species on the planet, the silica-based chemistry of diatom microshells limits their use in micro/nanodevice applications. However, the present work demonstrates that the silica-based chemistry of diatom microshells can be altered, without a loss of the 3-D shape or nanoscale features, through the use of gas/silica displacement reactions. By coupling the genetically-precise and massively-parallel self-assembly of diatoms (or other biomineralizing organisms) with such shape-preserving synthetic chemical conversion, micro/nanostructures with a wide variety of shapes and chemistries may be synthesized for a host of applications. The potential for genetic modification of diatoms to produce microshells with tailored shapes could be combined with shape-preserving chemical conversion to yield **G**enetically-**E**ngineered **M**icro/nanodevices (**GEMs**).

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"Genetically-Engineered Microdevices"

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A NOVEL HYBRID ROUTE TO CHEMICALLY-TAILORED, THREE-DIMENSIONAL OXIDE NANOSTRUCTURES: THE BASIC (BIOCLASTIC AND SHAPE-PRESERVING INORGANIC CONVERSION) PROCESS

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ABSTRACT

A novel, hybrid route to chemically-tailored oxide nanostructures with complex, three-dimensional (3D) shapes is introduced: the **B**ioclastic* and **S**hape-preserving **I**norganic **C**onversion (**BaSIC**) process. This process couples the massively-parallel and precise replication of biological organisms with rapid, shape-preserving chemical conversion via fluid/solid reactions, so that large numbers (billions) of identical 3D nanostructures can produced with desired (non-natural) compositions. The BASIC process is demonstrated by converting ornate, SiO_2-based diatom frustules (microshells) into MgO nanostructures that retain the frustule shapes and fine features. Such MgO nanostructures are attractive for biomedical and environmental applications (e.g., drug delivery, water purification). By choosing among the numerous shapes and fine features available in

*Bioclastic: *adj*; "of rock or similar material attaining its present form through the action of living organisms" [1]. "Bioclastic" is more appropriate than "biomimetic" for this process because a biological organism is actually being utilized (not just mimicked) to fabricate nanoparticle structures.

bioclastic structures (from diatoms, radiolaria, sponges, silicoflagellates, etc.), and by using other reactive gases, meso/nanostructures with a wide variety of shapes, features, and compositions may be mass produced by the BaSIC process.

INTRODUCTION

An increasing amount of international research and development activity is being devoted to the generation of miniature devices for a host of important applications in medicine (e.g., drug delivery capsules, membranes for protein separation or cell immuno-isolation), environmental protection (e.g., sensors for pollutants or pathogens, filters for waste water treatment), manufacturing (e.g., microrobots, mesoporous substrates for catalysis, microdies), telecommunications (e.g., microtransducers, positioning devices for optical fibers and lenses), and transportation (e.g., microcombustors, microengines) [2-9]. For optimal device performance in many of these applications, well-defined features (pores, channels, cavities, etc.) on the mesoscale (10^2 nm) or nanoscale (10^1 nm) are required. Much of the worldwide effort on micro/mesoscale fabrication has relied upon techniques developed for the microelectronics industry (e.g., the micromachining of silicon by lithographic methods or deep reactive ion etching) [2,3]. Unfortunately, these synthetic "top-down" approaches can not be easily adapted for the mass production of non-silicon devices with complex, three-dimensional (non-planar, curved) shapes and features on the mesoscale or nanoscale [3].

A wide variety of rigid microscopic structures with intricate, three-dimensional (3D) shapes and mesoscale-to-nanoscale features are generated by natural organisms [10]. Among the most ornate of such bioclastic structures are the frustules (microshells) of diatoms [10-13]. Diatoms (*Bacillariophyta*) are single-celled algae that are ubiquitous to marine and freshwater environments; indeed, diatoms are believed to account for up to one-fourth of the global primary production of carbon [7,11-14]. Diatoms form rigid cell walls (frustules) comprised of organic macromolecules and amorphous silica nanoparticles [14,15]. Each of the $\approx 10^5$ diatom species forms a frustule with unique shape and surface features [11,12]. Frustules may assume a variety of elongated (pennate) or radially-symmetric (centric) shapes, with maximum dimensions ranging from less than one micron to several hundreds of microns for various species [10-15]. The surfaces of diatom frustules possess fine features (pores, ridges, protuberances, etc.) arrayed in intricate patterns specific to a given species. These features possess dimensions ranging from the microscale scale to the nanometer

scale. The complex 3D structure of a given frustule can be replicated in large quantities by biological reproduction. The rate of diatom reproduction depends on a number of parameters (e.g., silicic acid concentration, nutrient concentration, temperature, light, etc.) [11-13,16]. Under proper conditions, diatom reproduction can occur several times per day, so that large numbers of frustules of identical shape may be produced in a relatively short period of time (e.g., 2^{30} = 1.07 billion similarly-shaped frustules would be generated in 10 days at a sustained reproduction rate of 3 times per day, or in 15 days at a sustained rate of 2 times per day). Such massively-parallel, precise, 3D self-assembly of silica nanoparticles under environmentally benign conditions is highly attractive for nanotechnological applications. However, the silica-based composition of diatoms severely limits the range of potential applications. Silica is not bioinert, nor is it chemically compatible with basic oxides or basic melts [14,17]. At high temperatures, amorphous silica exhibits poor creep resistance and is not structurally stable (due to crystallization).

A number of research groups have demonstrated that shaped macropreforms of silica or other oxides can be converted into new compositions, that retain the starting preform shape, through the use of displacement (oxidation-reduction) reactions with molten metals [18-24]. Breslin, et al. generated co-continuous composites of Al_2O_3 and Al-Si by immersing dense preforms of amorphous SiO_2 into molten Al at 1000-1300°C [18]. The reduction in solid volume associated with converting 3 moles of SiO_2 into 2 moles of Al_2O_3 provided additional internal volume for the molten Al-Si alloy, so that the final composite retained the shape of the starting dense SiO_2 preforms [18]. Loehman, et al. have also generated dense, near net-shaped Al_2O_3/Al-Si composites by exposing dense preforms of polycrystalline mullite, $Al_6Si_2O_{13}$, to molten Al or Al-Si [19]. Claussen, et al. have used gas pressure infiltration or squeeze casting to rapidly infiltrate porous oxide preforms (e.g., TiO_2, Nb_2O_5) with molten Al [20,21]. Reaction of the molten aluminum with the oxide generated co-continuous, near net-shaped composites of alumina with one or more aluminide compounds (e.g., Al_2O_3/$TiAl_3$, Al_2O_3/$NbAl_3$/Nb_2Al composites). Sandhage, et al. have also used reactive melt infiltration to convert porous ceramic-bearing preforms into new ceramic/metal composites of high density and near net shape [22-24]. In the latter case, displacement reactions were chosen that yielded an increase in solid ceramic volume, so that composites (e.g., MgO/Mg-Al, $MgAl_2O_4$/Fe-Ni-Al, ZrC/W) with relatively high ceramic contents (up to 86 vol%) could be directly produced.

The objective of this paper is to introduce a revolutionary new, hybrid nano-fabrication route: the **B**ioclastic and **S**hape-preserving **I**norganic **C**onversion (**BaSIC**) process [25]. Biologically self-assembled ceramic (bioclastic) nano-structures with complex 3D shapes are utilized as preforms in this process. Massively-parallel and precise biological reproduction may be used to generate large numbers (billions) of such preforms with identical shapes. With the BASIC process, such self-assembled nanostructures are converted into new compositions via shape-preserving reactions with fluids (gases or liquids). By coupling bioclastic self-assembly with near net-shape reaction processing, significant limitations encountered with top-down processing (difficulty in fabricating three-dimensional nanostructures with complex - nonplanar, curved - shapes) and bottom-up processing (very restricted range of self-assembled chemistries) can be avoided. The feasibility of the BaSIC process is demonstrated in this paper by converting diatom frustules (self-assembled, 3D, SiO_2 nanoparticle structures) into MgO nanostructures (e.g., for biomedical and environmental applications).

EXPERIMENTAL PROCEDURE

Diatoms were obtained in the form of diatomaceous earth (*Aulacoseira*, *Cyclotella*) or as algal cultures (*Cyclotella*, *Synedra*; Carolina Biological Supply Co., Burlington, NC). In the latter case, diatom culture growth was conducted in glass flasks sterilized in an autoclave. A 1 ml culture batch was added to 50 ml of an aqueous solution with appropriate growth media (Alga-Gro® freshwater medium for *Synedra*, Alga-Gro® seawater medium for *Cyclotella*; Carolina Biological Supply Co.) and sodium metasilicate as the silica source. Culture growth was allowed to proceed at 23°C for 21 days with a 12 hour light (fluorescent)/12 hour dark cycle. Prior to reaction with Mg(g), the diatomaceous earth and cultured diatoms were heated to 600°C for 8 hours in air to pyrolyze the organic material. The pyrolyzed frustules were then deposited onto a steel substrate. The substrate was placed inside a steel tube (internal dia. = 4.1 cm; internal length = 20.2 cm) along with 4-6 grams of magnesium, and the tube was then welded shut. The sealed tubes were then heated to 900°C and held for 4 hours in flowing argon (to minimize oxidation of the steel tube) within a tube furnace. After this heat treatment, the steel tube was cut open and the reacted frustules were removed. Secondary electron images of diatom frustules before and after reaction were obtained with a Model XL30 field emission gun scanning electron microscope (Philips Electron Instruments, Eindhoven, The Netherlands).

Cross-sections of reacted frustules were prepared with a focused ion beam instrument (Model Strata DB-235 System, FEI Company, Hillsboro, OR). Bright field images of such cross-sections were obtained with a CM-200T transmission electron microscope (Philips). The scanning and transmission electron microscopes were both equipped with a Si/Li energy-dispersive x-ray detector (Edax International, Mahwah, NJ) for microchemical analyses.

RESULTS AND DISCUSSION

Secondary electron images of the frustules of several pyrolyzed diatoms (*Synedra, Cyclotella, Aulacoseira*) are shown in Figure 1. *Synedra* frustules (Figs. 1a, 1b) possess the shape of flattened needles. The overlapping halves of the pennate *Synedra* frustule can be seen in Figure 1b*. The flat surfaces of these frustules are decorated with uniformly-spaced rows of fine pores (a few hundred nm in diameter) oriented in a direction perpendicular to the long needle axis. The diatom *Cyclotella* possesses a disk-shaped (centric) frustule (Fig. 1c) that consists of two overlapping, petri dish-shaped halves. The surface of this frustule is partially covered with narrow grooves (a few hundred nm in width) that radiate inward from the outside perimeter. The *Aulacoseira* frustule (Figs. 1d, 1e) consists of two capsule-shaped halves joined end-to-end so as to form a longer cylindrical assembly (one of these halves is shown in Fig. 2c below). One end of each capsule (half frustule) possesses a circular opening (Fig. 1e), whereas the other end (not shown) is closed and exhibits finger-like protuberances (see Fig. 2c) that interlock with those of another capsule to form the longer assembly. Regularly- spaced rows of fine pores (a few hundred nm in diameter) run along the cylindrical walls of the *Aulacoseira* frustule (Figs. 1d, e).

These diatom frustules were sealed within steel tubes, along with solid magnesium, and then heated to 900°C for 4 h. At this temperature, the magnesium melted and partially vaporized within the steel tubes (the equilibrium pressure of magnesium vapor over molten magnesium at 900°C is 0.16 atm [27]). Upon exposure to magnesium vapor, the silica within the diatoms underwent the following displacement (oxidation-reduction) reaction:

$$2Mg(g) + SiO_2(s) \Rightarrow 2MgO(s) + [Si] \quad (1)$$

*The frustule of each diatom is composed of two overlapping halves (note: the word "diatom" is derived from the Greek word "diatomos" which means "cut in half" [1]).

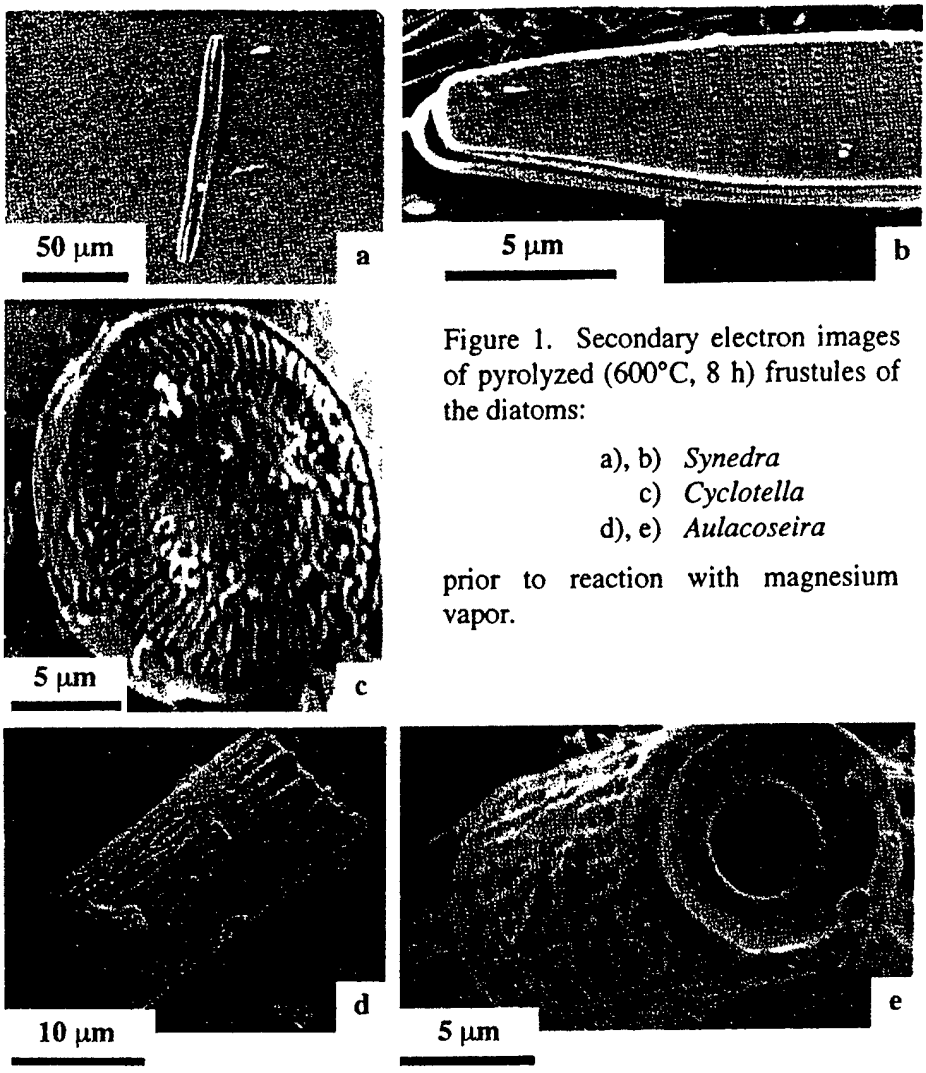

Figure 1. Secondary electron images of pyrolyzed (600°C, 8 h) frustules of the diatoms:

a), b) *Synedra*
c) *Cyclotella*
d), e) *Aulacoseira*

prior to reaction with magnesium vapor.

where [Si] refers to silicon dissolved within a Mg-Si liquid. The latter [Si] liquid formed by the continued reaction of gaseous magnesium with the elemental silicon generated upon the reduction of silica [26]. Thermodynamic calculations indicate that reaction (1) is strongly favored under these conditions [27]. Secondary electron images of reacted *Aulacoseira* and *Cyclotella* frustules are shown in Figure 2a and 2b, respectively. Although the frustule surfaces became more granular in appearance after reaction with Mg(g), the overall frustule shapes

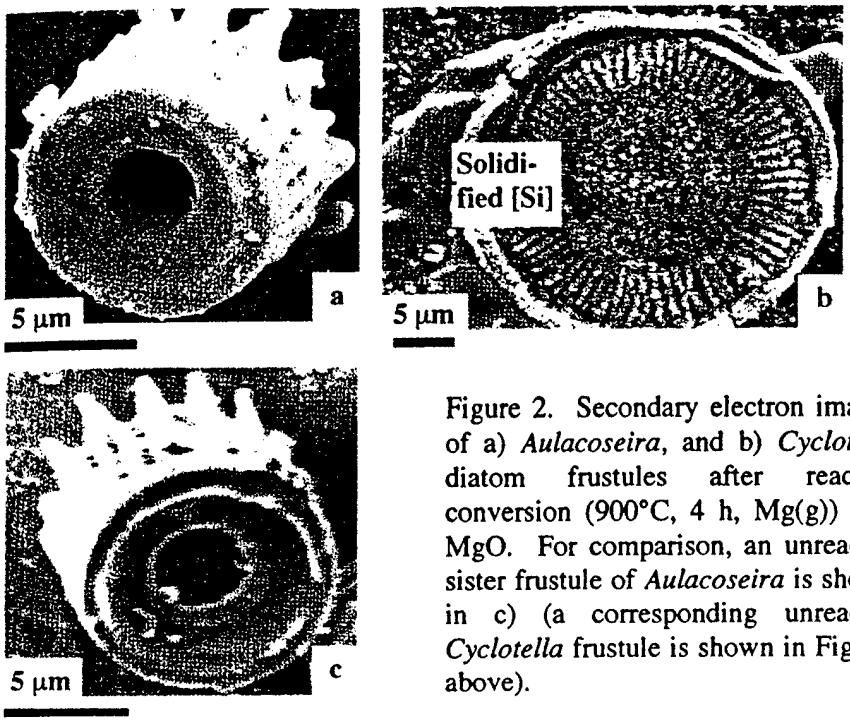

Figure 2. Secondary electron images of a) *Aulacoseira*, and b) *Cyclotella* diatom frustules after reactive conversion (900°C, 4 h, Mg(g)) into MgO. For comparison, an unreacted sister frustule of *Aulacoseira* is shown in c) (a corresponding unreacted *Cyclotella* frustule is shown in Fig. 1c above).

and fine features (mesoscale pores, grooves, protuberances) were retained. Energy-dispersive x-ray (EDX) analyses of the outside surfaces of these frustules during scanning electron microscopy revealed peaks for Mg and O, but not for Si, which was consistent with conversion of the SiO_2 into MgO. X-ray diffraction (XRD) analyses also yielded peaks for magnesia, but not for any crystalline silica polymorphs (such as quartz, cristobalite, or tridymite). The molten [Si] product of reaction (1) seeped out of the reacted frustules and solidified upon cooling. Such solidified [Si] can be seen below the reacted *Cyclotella* frustule in Fig. 2b. The reacted frustules could be easily plucked from this solidified Mg-Si (as was the case for the reacted *Aulacoseira* frustule shown in Fig. 2a).

The reacted frustules were also examined by transmission electron microscopy (TEM) in order to: i) evaluate the microstructure of the reaction product(s) and ii) determine whether unreacted silica was present below the magnesia detected on the frustule surface (note: subsurface amorphous silica can be difficult to detect by XRD or SEM/EDX analyses). Cross-sections of the wall of the reacted frustules were prepared by focused ion beam milling. Secondary electron images of a reacted *Aulacoseira* frustule at various stages of focused ion

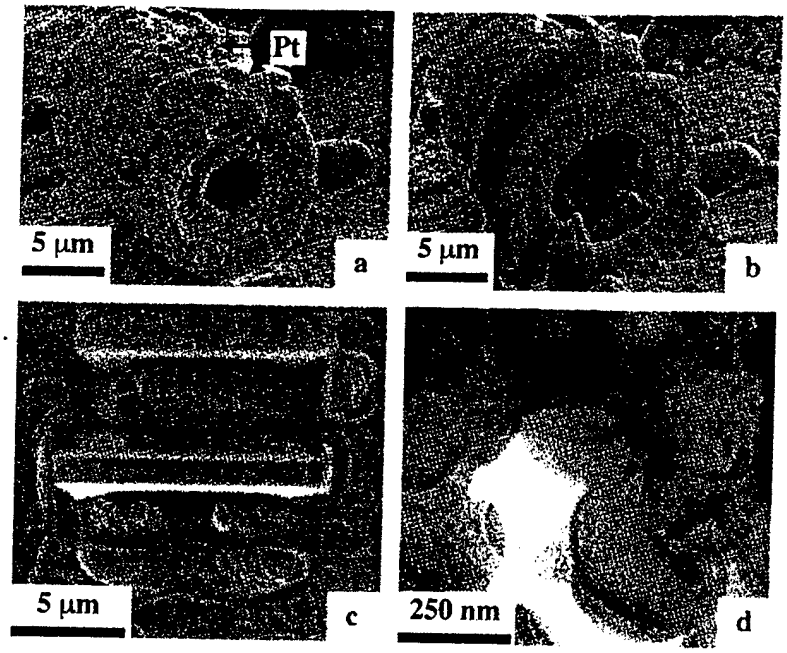

Figure 3. a), b), c) Secondary electron images of an *Aulacoseira* frustule after reaction for 4 h at 900°C with Mg(g). The image in a) reveals the frustule after deposition of a Pt coating. Side and top-down views of the wafer-shaped cross-section cut out by the focused ion beam are shown in b) and c). A bright field TEM image of this cross-section is shown in d).

beam milling are shown in Figs. 3a-c. The reacted frustule was first coated with a layer of platinum (Fig. 3a) in order to avoid fragmentation of the cross-section during milling. A focused ion beam was then used to remove material from both sides of a wafer-shaped cross-section, as shown in Figs. 3b and 3c. A bright field TEM image obtained from this cross-section is shown in Fig. 3d. Round grains with diameters of a few hundred nanometers were observed throughout the cross-section, which was consistent with the grain morphology observed on the surface of the reacted frustule by scanning electron microscopy (see Fig. 2a). TEM/EDX analyses of these rounded grains revealed peaks for Mg and O, but not for Si. The absence of silicon throughout the specimen cross-section confirmed that: i) the conversion of SiO_2 to MgO by reaction (1) was completed within 4 h at 900°C, and ii) the liquid [Si] product of this reaction had completely seeped out of the frustule during this heat treatment, apparently due to poor wetting with MgO.

Such poor wetting was also consistent with the weak adhesion of the solidified [Si] with the converted (MgO) frustules.

This work demonstrates the feasibility of the BASIC process. Biogenic oxide nanoparticle assemblies with complex three-dimensional shapes can be converted, via gas/solid reactions, into new compositions while retaining the same shapes and fine features. The mesoporous magnesia structures generated in the present work are attractive for a variety of uses, including: i) bioinert microcapsules for delivering very small doses of medication, ii) efficient filters for removing heavy metals from waste water, or for separating fine contaminant particles from basic fluids, iii) fine scale, controlled-shape (needles, tubes, disks, etc.), light weight (ρ[MgO] = 3.58 g/cm^3) filler or reinforcement phases for polymer-matrix composites, and iv) high-surface-area, chemically-compatible substrates for catalytic syntheses of certain petrochemicals [28-30].

Although the focus of this paper has been the shape-preserving conversion of certain diatom frustules into magnesia, the BASIC process is certainly not limited to these preforms or to MgO-based components. Self-assembled, three-dimensional bioclastic meso/nanostructures with a wide variety of other shapes, fine features, and chemistries could also be chemically modified (e.g., nanostructures of: silica from radiolaria, silicoflagellates, sponges; iron oxide from chiton teeth or bacteria; manganese oxides from fungi [12,31]). Other gaseous reactants than magnesium (e.g., reactive halides, organometallics, or other elemental gases) could be used in the conversion process to generate a host of oxide or oxide/metal products. Given such a large selection of possible shapes and chemical reactions, the BASIC process could be used to produce a multitude of meso/nanostructures with desired compositions for optimal electromagnetic, optical, thermal, chemical, or mechanical properties.

A wide diversity of frustule shapes, sizes, and fine surface features exists among the $\approx 10^5$ diatom species [11,12]. Given such natural variations in frustule geometry, it seems likely that many non-existing genomic modifications of diatom frustules may also be viable. If future genetic engineering yields frustules with tailored shapes and features (e.g., microneedles, micronozzles, microbearings, microchambers, etc.), then the shape-preserving gas/solid reactions of the type discussed in the present paper could be used to convert such shape-tailored preforms into preferred compositions for particular microdevice applications. Indeed, a unique coupling of genetic tailoring, biological replica-

CONCLUSIONS

Nanoparticle assemblies with complex 3D shapes and tailored chemistries have been fabricated by a novel, hybrid route: the BaSIC (Bioclastic and Shape-preserving Inorganic Conversion) process. With this process, biologically self-assembled ceramic (bioclastic) nanostructures can be converted into new compositions via the use of shape-preserving gas/solid reactions. To demonstrate this process, diatom microshells (i.e., silica nanoparticle assemblies) have been converted into magnesia. Several diatom species (*Aulacoseira*, *Cyclotella*, *Synedra*) with pennate or centric microshells (frustules) were obtained from algal cultures or as diatomaceous earth. After removal of organic material by pyrolysis, the frustules were exposed to magnesium vapor at 900°C. The Mg(g) underwent a displacement (oxidation-reduction) reaction with the amorphous SiO_2 in the frustules to yield MgO and Si dissolved in a Mg-rich liquid. The Mg-Si liquid seeped out of the frustule during the course of reaction (this liquid did not wet the MgO), so that the SiO_2 frustule was converted directly into MgO. TEM analyses indicated that the displacement reaction was completed within 4 h at 900°C. The resulting MgO nanoparticle assemblies retained the shapes and fine features (mesoscale pores, ridges, protuberances) of the starting frustules. Such MgO nanoparticle structures are attractive as mesoporous filters, mesoporous microcapsules, microfillers/reinforcements, and catalyst substrates for medical, environmental, and manufacturing applications. By choosing among numerous natural bioclastic nanostructures and reactant gases, the BASIC process could be used to produce meso/nanostructures with a wide variety of shapes, surface features, and compositions. Furthermore, if future genetic engineering of mineral-forming organisms yields bioclastic nanostructures with tailored shapes, then synergistic coupling of such genetic manipulation with the BASIC process would allow for the mass production of Genetically Engineered Microdevices (GEMs) for numerous domestic and military applications.

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